

SYNTHESIS AND CHARACTERISATION OF HRuRh₃(CO)₁₂. CRYSTAL STRUCTURES OF HRuRh₃(CO)₁₂, HRuRh₃(CO)₁₀(PPh₃)₂ AND HRuCo₃(CO)₁₀(PPh₃)₂

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(Received January 29th, 1985)

Summary

A new ruthenium-rhodium mixed-metal cluster HRuRh₃(CO)₁₂ and its derivatives HRuRh₃(CO)₁₀(PPh₃)₂ and HRuCo₃(CO)₁₀(PPh₃)₂ have been synthesized and characterized. The following crystal and molecular structures are reported: HRuRh₃(CO)₁₂: monoclinic, space group $P2_1/c$, a 9.230(4), b 11.790(5), c 17.124(9) Å, β 91.29(4)°, $Z = 4$; HRuRh₃(CO)₁₀(PPh₃)₂ · C₆H₁₄: triclinic, space group $P\bar{1}$, a 11.777(2), b 14.079(2), c 17.010(2) Å, α 86.99(1), β 76.91(1), γ 72.49(1)°, $Z = 2$; HRuCo₃(CO)₁₀(PPh₃)₂ · CH₂Cl₂: triclinic, space group $P\bar{1}$, a 11.577(7), b 13.729(7), c 16.777(10) Å, α 81.39(4), β 77.84(5), γ 65.56°, $Z = 2$. The reaction between Rh(CO)₄⁻ and (Ru(CO)₃Cl₂)₂ in tetrahydrofuran followed by acid treatment yields HRuRh₃(CO)₁₂ in high yield. Its structural analysis was complicated by a 80–20% packing disorder. More detailed structural data were obtained from the fully ordered structure of HRuRh₃(CO)₁₀(PPh₃)₂, which is closely related to HRuCo₃(CO)₁₀(PPh₃)₂ and HFeCo₃(CO)₁₀(PPh₃)₂. The phosphines are axially coordinated.

Introduction

The synthesis, characterisation, and catalytic properties of mixed-metal cluster compounds have been intensively studied [1]. Little is known, however, about ruthenium-rhodium mixed-metal clusters. Structural information is available for a basic hydride cluster, H₂Ru₂Rh₂(CO)₁₂ [2], an anionic cluster, RuRh₄(CO)₅²⁻ [3], and a more complicated phosphine complex, Ru₃Rh₂(μ₄-PPh)(CO)₁₃(PEt₃) [4]. The synthesis and isolation of Ru₃RhH(μ₃-PPh)(CO)₁₀(PR₃) (R = Et or Ph) has been

also reported [4]. Knifton proposed an empirical formula of $\text{Ru}_2\text{Rh}(\text{CO})_{12}$ for a cluster isolated from a solution obtained in a catalysed ethylene glycol synthesis [5]. Ruthenium–rhodium bonds have been identified by Chaudret et al. in the bimetallic phosphine complexes $\text{RuRhCl}(\mu\text{-CO})(\text{CO})_2(\text{dppm})_2$ and $\text{RuRhClH}_2(\mu\text{-CO})(\text{CO})(\text{dppm})_2$ [6]. In the present work a new ruthenium-rhodium mixed-metal cluster $\text{HRuRh}_3(\text{CO})_{12}$ has been synthesized and characterized. The cluster belongs to the class of hydride clusters $\text{HMM}'_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}, \text{Ru}$ or Os and $\text{M}' = \text{Co}, \text{Rh}$ or Ir), of which only cobalt clusters $\text{HFeCo}_3(\text{CO})_{12}$ [7], $\text{HRuCo}_3(\text{CO})_{12}$ [8] and $\text{HOsCo}_3(\text{CO})_{12}$ [9] are known; such metal hydrides are obtained from the corresponding anionic clusters by acid treatment. The synthesis of the corresponding rhodium derivatives have been attempted; Ceriotti et al. found $\text{FeRh}_3(\text{CO})_{12}^-$ to be too unstable for even spectroscopic characterisation [10], but, the crystal structure of $\text{FeRh}_3(\mu\text{-PPh}_2)_3(\text{CO})_{12}$ has been determined [11].

In the present study the crystal structure of $\text{HRuRh}_3(\text{CO})_{12}$ was found to be disordered, which prevented collection of detailed structural information.

To permit detailed geometry comparisons with related clusters the phosphine derivatives $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$ and $\text{HRuCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$ were synthesized and characterized by X-ray diffraction. Structural comparison with $\text{HFeCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$ [12] reveals trends in the variation of the geometry of ligand replacement in the $\text{HMM}'_3(\text{CO})_{12}$ clusters.

Experimental

Reagents

$\text{Rh}_2(\text{CO})_4\text{Cl}_2$, $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$, $(\text{Ru}(\text{CO})_3\text{Cl}_2)_2$ and PPh_3 were purchased from Ventron Corp. and were used without further purification.

$\text{Rh}(\text{CO})_4^-$ -salts [13,14] and $\text{HRuCo}_3(\text{CO})_{12}$ [15] were prepared by published procedures. Tetrahydrofuran (THF) was dried and deoxygenated by stirring over $\text{Na}/\text{benzophenone}$ ketyl, and freshly distilled before use. Other solvents were deoxygenated by bubbling N_2 through them. Reactions and manipulations were carried under N_2 up to the stage of chromatographic separations.

Syntheses

$\text{HRuRh}_3(\text{CO})_{12}$. Reaction of $(\text{Ru}(\text{CO})_3\text{Cl}_2)_2$ (63 mg, 0.12 mmol) with a freshly-prepared solution of $\text{NaRh}(\text{CO})_4$ [13] (made from 239 mg, 0.61 mmol $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ and used without purification) in THF at room temperature gave a greenish solution. The Ru/Rh ratio was approximately 1/3. After 1 h the solvent was evaporated in vacuo and the solid residue was treated with 20% H_3PO_4 to give the hydride cluster, which was extracted into hexane. Infrared spectra showed small amounts of impurities to be present, and of these $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}$ and tetranuclear ruthenium clusters were identified. An attempted chromatographic separation on silica gel failed because of a rapid decomposition to $\text{Rh}_6(\text{CO})_{16}$.

Attempts to separate $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}$ by fractional crystallisation from hexane or CH_2Cl_2 at -40°C also failed. The amount of the impure product (113 mg) represents ca. 60% yield.

$\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$. A microscale synthesis was carried out using the procedure described by Bruce et al. [16]. The $\text{HRuRh}_3(\text{CO})_{12}$ cluster and PPh_3 (2 molar equivalents) were dissolved in THF and the Ph_2O^- catalyst (0.02 M THF solution)

was added dropwise through a rubber septum. After 1 h the THF was evaporated and the residue was then separated on silica gel. An orange-red band was eluted with CH_2Cl_2 hexane (1/5) as the only cluster product.

$\text{HRuCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$. A crude phosphine product obtained by a procedure similar to that in the preceding experiment was chromatographed on silica gel with CH_2Cl_2 hexane as eluent. A yellow band was followed by a violet band of the title compound. (Elution with CH_2Cl_2 then yielded a larger amount of another, still uncharacterized phosphine compound as a red band.) The yield was 25%.

X-ray crystallography

Crystals were grown by slow evaporation from saturated CH_2Cl_2 /hexane solutions. The data for the compounds were collected on a Nicolet R3m diffractometer. Accurate cell parameters were obtained from 16–22 centered reflections in the range $15^\circ < 2\theta < 25^\circ$. Intensities were corrected for background, polarization, and Lorentz factors. Empirical absorption corrections were made from ψ -scan data. The structures of $\text{HRuRh}_3(\text{CO})_{12}$ and $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh})_2$ were solved by direct methods from the SHELXTL program package [17], whereas for $\text{HRuCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$ the atomic coordinates of the isomorphous $\text{HFeCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$ [12] were used for refinement. The organic hydrogen atoms were placed in ideal positions. In $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$ the cluster hydrogen was directly located and refined isotropically. In other structures the hydrogen positions were deduced indirectly from the cluster geometry. In $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$ metal atoms were assigned from difference Fourier maps. The structure was first refined close to the final anisotropic values. Several combinations of ruthenium and rhodium atoms were then assigned

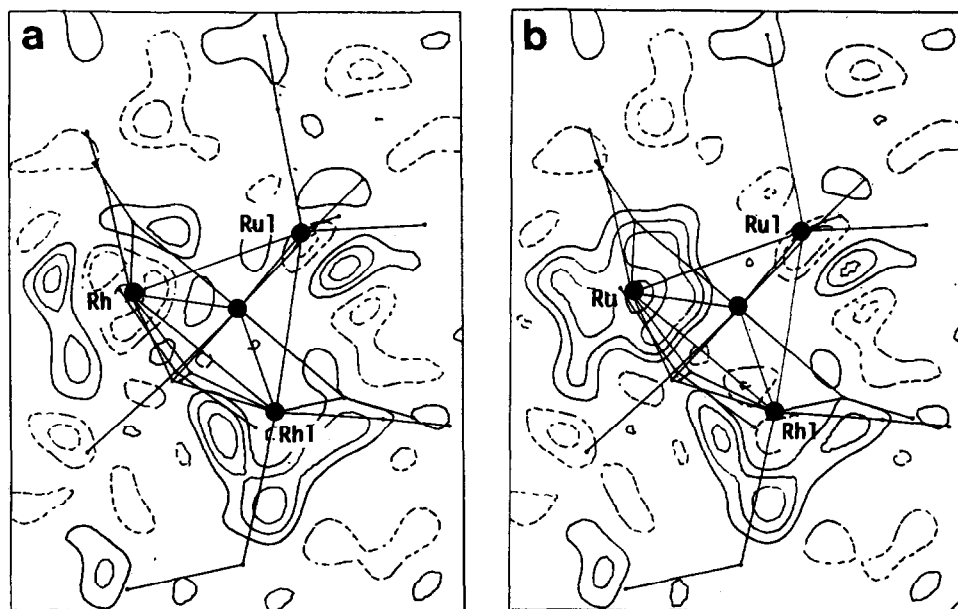


Fig. 1. Difference Fourier maps after calculations, where Rh(3) position is occupied by Rh (a) or Ru (b). The marked three metals define the plane of the map.

TABLE 1
INFRARED SPECTRA

	Solvent	$\nu(\text{CO})$ (cm^{-1})
$\text{HRuRh}_3(\text{CO})_{12}$	n-hexane	2106w, 2077s, 2067vs, 2036m, 2012m, 1917m, 1883m
$\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$	n-hexane	2079m, 2066s, 2037s, 2020s, 1982m, 1900m, 1870m, 1845m
$\text{HRuCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$	CH_2Cl_2	2083s, 2049vs, 2038s, 2012s, 1960w, 1897w, 1868m, 1850m

for the metals of the cluster tetrahedron. Each model was analyzed by difference Fourier maps of the faces of the tetrahedron. Figure 1a shows an example in which the metal assignment is correct. The surroundings of the metal atoms have small positive and negative fluctuations. Figure 1b shows the same cluster plane, but with Rh(3) refined as Ru. The map is unchanged except around Ru, where there is a uniform excess electron density with a radius about 1.2 Å. X-ray data of good quality and low residuals ($R = 0.03\%$) are essential for the analysis. After an anisotropic refinement for non-hydrogen atoms and an isotropic refinement for hydrogen atoms the structures converged to $R = 0.121$ and $R_w = 0.125$ for $\text{HRuRh}_3(\text{CO})_{12}$, $R = 0.0280$ and $R_w = 0.0304$ for $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$ and $R = 0.0654$ and $R_w = 0.0608$ for $\text{HRuCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$. The high R value for $\text{HRuRh}_3(\text{CO})_{12}$ is due to the 80–20% packing disorder: only the metals were refined for the 20% cluster. Full lists of bond lengths and angles, thermal parameters, and structure factors may be obtained from the authors.

X-ray fluorescence

The X-ray fluorescence analysis was performed by JEOL 35 CF Scanning Electron Microscope equipped with LINK energy dispersive semiconductor X-ray detector. Single purified crystals were used as samples to avoid any problems caused by inhomogeneity.

Infrared spectroscopy

Infrared spectra were recorded in n-hexane or CH_2Cl_2 on a Perkin-Elmer 297 infrared Spectrophotometer using 0.5 mm NaCl cells. The data are given in Table 1.

Results and discussion

The complexes $\text{HRuCo}_3(\text{CO})_{12}$ and $\text{HRuRh}_3(\text{CO})_{12}$ can be prepared by the same type of procedure, in which the metallate anion $\text{M}(\text{CO})_4^-$ ($\text{M} = \text{Rh}$ or Co) is treated with $(\text{Ru}(\text{CO})_3\text{Cl}_2)_2$ in THF. The hydrides are then produced by acid treatment. Use of $(\text{Ru}(\text{CO})_3\text{Cl}_2)_2$ is particularly effective since in THF the chlorine bridges are broken and reactive mononuclear ruthenium species are formed [18]. Reactions of $\text{KRh}(\text{CO})_4$ [14] with RuCl_3 or $(\text{Ru}(\text{CO})_3\text{Cl}_2)_2$ did not produce $\text{HRuRh}_3(\text{CO})_{12}$. (The metallation solution must not contain water or hydroxide residues, which are extracted into THF from the KOH/DMSO medium used in the $\text{KRh}(\text{CO})_4$ synthesis.) When $\text{KRh}(\text{CO})_4$ was used, the main product after acid treatment was $\text{RuRh}_5(\text{CO})_{16}^-$ [19]. This together with the decomposition of $\text{HRuRh}_3(\text{CO})_{12}$ to $\text{Rh}_6(\text{CO})_{16}$ during chromatographic separation indicates that RuRh_3 clusters readily condense to hexanuclear species; this has been suggested also as the reason for the

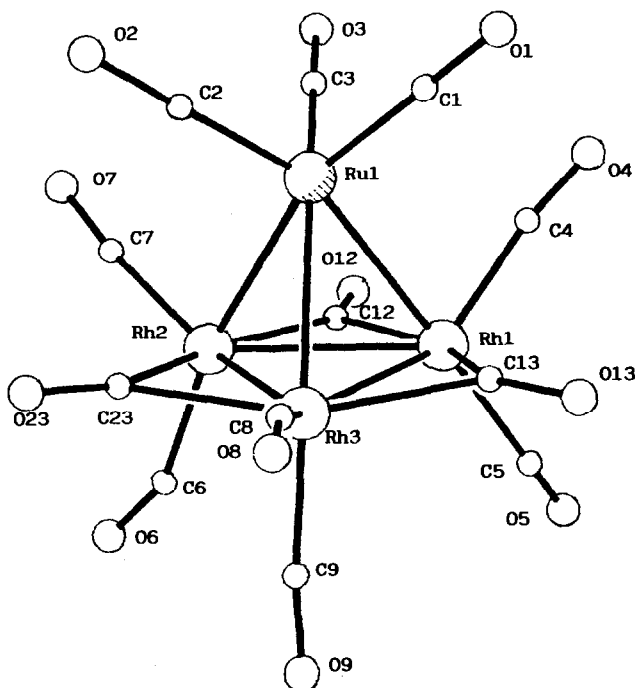


Fig. 2. Structure and numbering scheme for $\text{HRuRh}_3(\text{CO})_{12}$.

instability of $\text{FeRh}_3(\text{CO})_{12}^-$ [10]. In contrast $\text{HRuRh}_3(\text{CO})_{12}$ is, relatively air-stable, and its crystal structure could be determined.

Crystal structures of $\text{HRuRh}_3(\text{CO})_{12}$, $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$ and $\text{HRuCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$

The numbering schemes of the metal clusters are given in Figs. 2, 4 and 5. The phosphine groups replace carbonyls 5 and 6 in $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$ and $\text{HRuCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$. Crystallographic data are given in Table 2 and atomic coordinates in Table 3.

The structure analysis of $\text{HRuRh}_3(\text{CO})_{12}$ was complicated by the packing disorder (ca. 80–20%) (Fig. 3), which did not allow direct location of the hydrogen atom. $\text{HRuRh}_3(\text{CO})_{12}$ crystallises in the same space group $P2_1/c$ as $\text{Rh}_4(\text{CO})_{12}$, with slightly different unit cell parameters [20]. The cluster core (Fig. 1) with three bridging carbonyls is common to most tetranuclear dodecacarbonyl clusters of iron and cobalt groups. There is direct and indirect evidence for the detailed structure of $\text{HRuRh}_3(\text{CO})_{12}$. Elemental analysis by X-ray fluorescence gives an approximately 1/3 Ru/Rh ratio, establishing the RuRh_3 stoichiometry for the cluster core. The cluster geometry suggests that the hydrogen atom bridges the Ru(1)–Rh(3) bond. A bridging hydride lengthens the metal–metal bond and has a repulsive effect on the carbonyl groups (Tables 4 and 5). The Ru(1)–Rh(3) bond length (2.878 Å) is very close to the hydride-bridged metal–metal bond lengths in $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}$ (2.889 and 2.920 Å), but considerably longer than the non-bridged Ru–Rh bond in the same molecule (2.730 Å). Similar bond lengthening is known in tetraruthenium

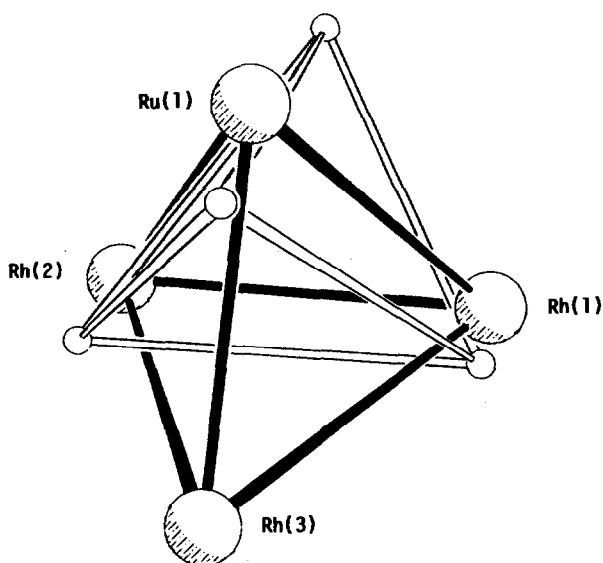


Fig. 3. The 80-20% packing disorder in $\text{HRuRh}_3(\text{CO})_{12}$.

clusters: in $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ and $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ the long hydride bridged distances average 2.950 and 2.930 Å, and the short non-bridged distances average 2.786 and 2.783 Å, respectively. The bridging hydrogen influences the geometry of the carbonyls

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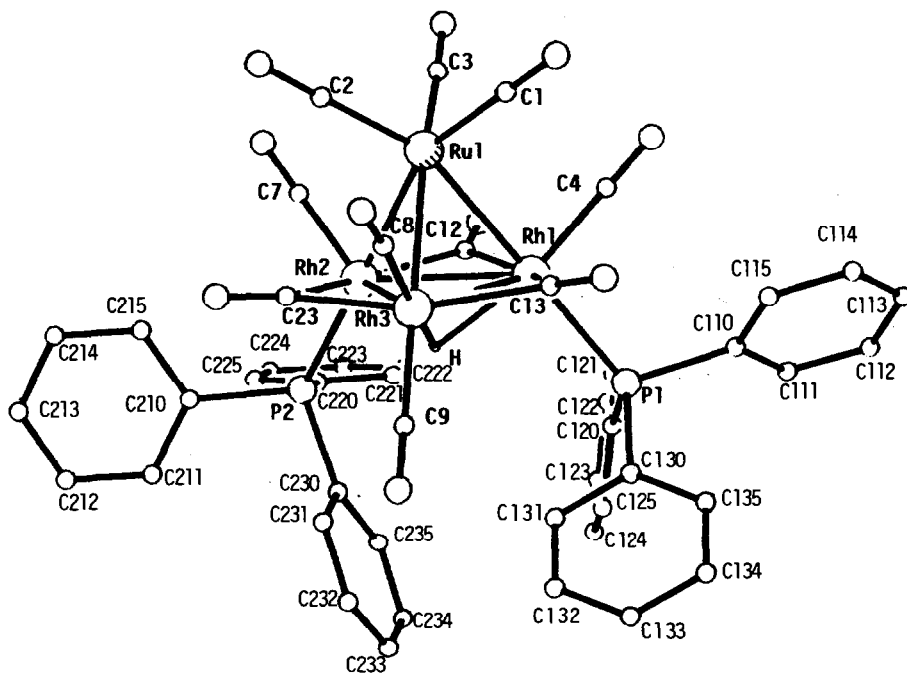


Fig. 4. Structure and numbering scheme for $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$.

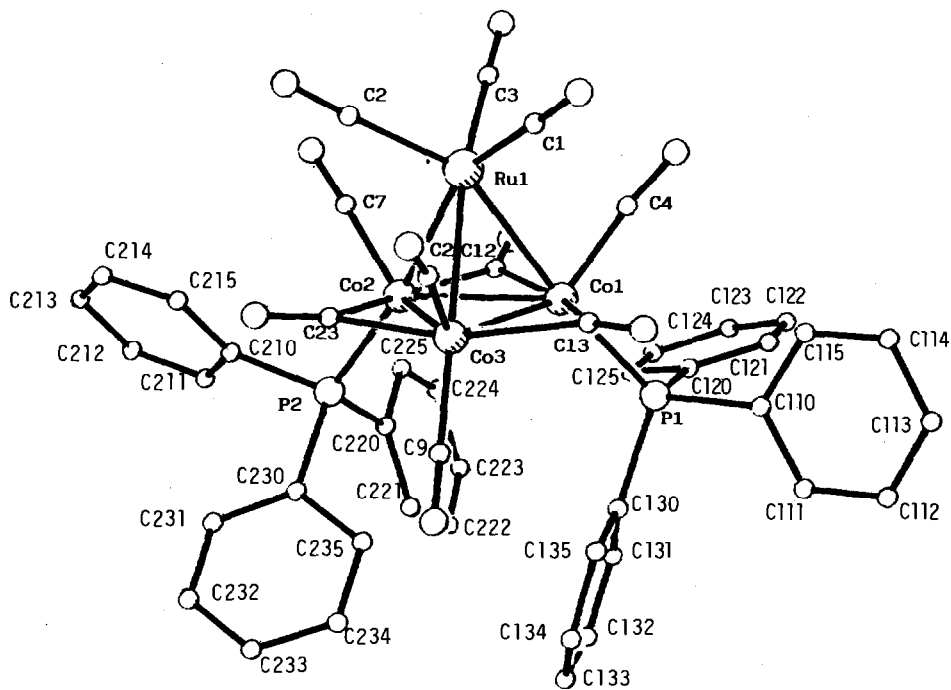


Fig. 5. Structure and numbering scheme for $\text{HRuCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$.

TABLE 2

CRYSTALLOGRAPHIC DATA

Formula	$\text{HRuRh}_3(\text{CO})_{12}$	$\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2 \cdot \text{C}_6\text{H}_{14}$	$\text{HRuCo}_3(\text{CO})_{10}(\text{PPh}_3)_2 \cdot \text{CH}_2\text{Cl}_2$
Formula weight	746.9	1301.7	1168.6
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.230(4)	11.777(2)	11.577(7)
b (Å)	11.790(5)	14.079(2)	13.729(7)
c (Å)	17.124(9)	17.010(2)	16.777(10)
α (deg)	90	86.99(1)	81.39(4)
β (deg)	91.29(4)	76.91(1)	77.84(5)
γ (deg)	90	72.49(1)	65.56(4)
V (Å) ³	1863(1)	2619(6)	2367(2)
Z	4	2	2
D_{calcd} (g cm ⁻³)	2.66	1.65	1.64
Crystal dimensions (mm)	0.3 × 0.1 × 0.1	0.4 × 0.3 × 0.2	0.4 × 0.2 × 0.1
Radiation	Mo- K_α	Mo- K_α	Mo- K_α
Monochromator	graphite	graphite	graphite
2 θ -limits	5–50	5–50	3–45
No. of refl. measured	3258	9205	6131
No. of unique data	2426	7316	3154
μ (Mo- K_α) (cm ⁻¹)	33.7	13.0	16.2
R^b	0.121	0.028	0.065
R_w^c	0.125	0.030	0.061

^a $|F| > 5\sigma(|F|)$. ^b $R = \sum \|F_o| - |F_c|\| / \sum |F_o|$. ^c weight = $1/(\sigma^2(F) + 0.005F^2)$.

TABLE 3

ATOM COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS ($\text{\AA}^2 \times 10^3$) FOR $\text{HRuRh}_3(\text{CO})_{12}$,
 $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$ AND $\text{HRuCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$

Atom	x	y	z	U^a
<i>HRuRh₃(CO)₁₂</i>				
Ru(1)	8162(3)	1556(3)	1167(2)	37(1)
Rh(1)	7745(6)	3843(4)	1109(2)	39(1)
Rh(2)	7026(3)	2603(2)	2439(2)	37(1)
Rh(3)	5293(4)	2513(4)	1114(2)	35(1)
O(1)	9127(34)1	1104(23)	-498(20)	115(14)
O(2)	7572(28)	-996(23)	1584(19)	92(12)
O(3)	11260(29)	1641(31)	1854(19)	110(14)
O(4)	11558(36)	3774(29)	323(20)	119(16)
O(5)	7462(37)	6260(30)	1205(22)	126(17)
O(6)	5727(31)	3835(26)	3810(18)	90(12)
O(7)	8907(28)	1196(25)	3531(20)	100(13)
O(8)	3087(44)	1300(33)	184(20)	135(18)
O(9)	3189(41)	4302(35)	1639(21)	137(18)
O(12)	9741(28)	4138(21)	2557(17)	84(11)
O(13)	6018(33)	3682(28)	-482(18)	98(13)
O(23)	4484(35)	816(25)	2440(17)	94(12)
C(1)	8756(49)	1289(35)	144(23)	86(17)
C(2)	7793(44)	72(36)	1407(28)	86(18)
C(3)	10008(40)	1557(37)	1551(22)	75(15)
C(4)	9518(47)	3724(37)	657(24)	86(18)
C(5)	7406(36)	5444(20)	1081(25)	70(14)
C(6)	6116(33)	3581(41)	3187(32)	103(20)
C(7)	8100(33)	1687(26)	3117(23)	64(13)
C(8)	4018(46)	1568(34)	495(24)	96(16)
C(9)	3936(44)	3575(41)	1458(30)	104(20)
C(12)	8707(51)	3750(43)	2255(26)	99(20)
C(13)	6474	3511(34)	274(26)	102(18)
C(23)	5279(44)	1565(32)	2241(24)	77(15)
Ru(1*)	5313(43)	2499(23)	1567(57)	412(53)
Ru(2*)	7915(29)	3856(34)	1364(37)	213(29)
Ru(3*)	8035(32)	1446(27)	1470(46)	341(39)
Ru(4*)	6958(25)	2562(16)	170(28)	200(23)
<i>HRuRh₃(CO)₁₀(PPh₃)₂</i>				
Ru(1)	2900(1)	2554(1)	3203(1)	51(1)
Rh(1)	4575(1)	3558(1)	2866(1)	40(1)
Rh(2)	4992(1)	1749(1)	2074(1)	44(1)
Rh(3)	5027(1)	1791(1)	3706(1)	44(1)
P(1)	6035(1)	4442(1)	2714(1)	41(1)
P(2)	6842(1)	995(1)	1136(1)	50(1)
O(1)	1293(3)	3815(3)	4649(3)	114(2)
O(2)	1908(4)	797(3)	3547(3)	114(2)
O(3)	1223(4)	3499(3)	2086(3)	122(2)
O(4)	2471(4)	5387(3)	2922(4)	143(3)
O(7)	3281(3)	1231(3)	1234(2)	108(2)
O(8)	3527(4)	1047(3)	5139(2)	116(2)
O(9)	7342(3)	926(3)	4358(2)	95(2)
O(12)	4172(4)	3667(2)	1154(2)	92(2)
O(13)	4216(3)	3727(2)	4698(2)	78(1)
O(23)	5233(4)	-220(2)	2961(2)	99(2)

TABLE 3 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ^a
C(1)	1903(4)	3326(4)	4120(3)	74(2)
C(2)	2290(4)	1420(3)	3421(3)	72(2)
C(3)	1858(4)	3150(4)	2507(3)	74(2)
C(4)	3244(4)	4692(3)	2926(3)	75(2)
C(7)	3919(4)	1422(3)	1561(3)	69(2)
C(8)	4044(4)	1358(3)	4593(3)	69(2)
C(9)	6549(4)	1259(3)	4066(3)	59(2)
C(12)	4512(4)	3231(3)	1687(3)	60(2)
C(13)	4485(4)	3309(3)	4092(2)	50(1)
C(23)	5165(4)	606(3)	2831(9)	63(2)
C(110)	5338(3)	5750(2)	3035(2)	48(1)
C(111)	5714(5)	6506(3)	26111(3)	70(2)
C(112)	5220(5)	7477(3)	2894(3)	88(2)
C(113)	4326(5)	7703(3)	3600(3)	84(2)
C(114)	3958(4)	6962(3)	4021(3)	72(2)
C(115)	4456(4)	5991(3)	3745(3)	59(2)
C(120)	6909(4)	4521(3)	1693(2)	51(2)
C(121)	6271(5)	4915(3)	1105(3)	76(2)
C(122)	6880(7)	5036(4)	330(3)	104(3)
C(123)	8134(7)	4741(4)	132(3)	110(3)
C(124)	8752(6)	4338(4)	697(3)	99(3)
C(125)	8175(4)	4236(3)	1478(3)	67(2)
C(130)	7170(3)	3999(3)	3321(2)	44(1)
C(131)	7872(4)	3008(3)	3255(3)	57(2)
C(132)	8715(4)	2646(3)	3721(3)	66(2)
C(133)	8882(4)	3255(4)	4254(3)	69(2)
C(134)	8201(5)	4227(4)	4324(3)	77(2)
C(135)	7348(4)	4608(3)	3866(3)	62(2)
C(210)	7150(5)	-349(3)	977(2)	62(2)
C(211)	8303(5)	-998(3)	879(3)	82(2)
C(212)	8505(7)	-2008(4)	742(4)	104(3)
C(213)	7577(8)	-2357(4)	646(4)	114(4)
C(214)	6411(7)	-1727(4)	787(4)	111(4)
C(215)	6203(5)	-714(4)	937(3)	87(2)
C(220)	6947(4)	1487(3)	119(2)	53(2)
C(221)	6786(5)	2492(3)	5(3)	75(2)
C(222)	6828(5)	2891(4)	-758(3)	84(2)
C(223)	7024(5)	2297(4)	-1414(3)	87(3)
C(224)	7162(6)	1299(4)	-1312(3)	95(3)
C(225)	7141(5)	884(4)	-550(3)	79(2)
C(230)	8225(4)	1046(3)	1427(2)	54(2)
C(231)	8459(4)	598(3)	2140(3)	65(2)
C(232)	9503(5)	598(4)	2386(3)	81(2)
C(233)	10287(5)	1057(4)	1936(4)	87(3)
C(234)	10060(5)	1517(5)	1246(4)	95(3)
C(235)	9038(5)	1519(4)	987(3)	75(2)
C(1*) ^c	476(10)	8863(7)	4270(6)	232(8)
C(2*) ^c	493(21)	8205(15)	3694(11)	316(13)
C(3*) ^c	-550(11)	8079(13)	3645(11)	380(12)
C(4*) ^c	-352(22)	7356(19)	2976(17)	498(22)
C(5*) ^c	-1141(20)	7022(21)	3087(15)	397(16)
C(6*) ^c	-607(13)	6111(10)	2400(10)	279(11)
H(1)	5732(32)	2236(25)	2769(20)	66(9)

TABLE 3 (continued)

Atom	x	y	z	U^a
<i>HRuCo₃(CO)₁₀(PPh₃)₂</i>				
Ru(1)	1849(1)	2341(1)	1810(1)	45(1)
Co(1)	-396(2)	3151(1)	2791(1)	38(1)
Co(2)	136(2)	1470(1)	2098(1)	36(1)
Co(3)	-381(2)	3237(1)	1282(1)	38(1)
P(1)	-2194(4)	3953(3)	3684(2)	42(2)
P(2)	-1139(3)	5841(3)	2197(2)	40(2)
O(1)	2654(10)	4197(8)	1395(7)	83(6)
O(2)	3665(11)	1061(10)	370(8)	95(7)
O(3)	3677(11)	1149(11)	3023(7)	106(7)
O(4)	1290(10)	3459(10)	3681(8)	93(7)
O(7)	2475(9)	-425(8)	2143(8)	85(6)
O(8)	1232(11)	3855(9)	-82(7)	79(6)
O(9)	-2658(10)	4396(8)	498(7)	79(6)
O(12)	383(10)	1120(7)	3835(6)	67(5)
O(13)	-791(11)	5261(8)	1933(6)	71(6)
O(23)	529(10)	1357(7)	326(5)	64(5)
C(1)	2331(13)	3479(12)	1577(9)	55(8)
C(2)	3000(16)	1550(13)	853(12)	72(10)
C(3)	3010(15)	1573(12)	2587(9)	63(8)
C(4)	683(13)	3297(11)	3314(9)	57(7)
C(7)	1593(13)	348(12)	2098(9)	57(8)
C(8)	671(14)	3577(11)	496(10)	51(8)
C(9)	-1842(13)	3923(11)	829(8)	53(7)
C(12)	1001(13)	1626(11)	3223(8)	49(7)
C(13)	-612(15)	4377(13)	2037(9)	57(8)
C(23)	217(13)	1763(10)	947(8)	44(7)
C(110)	-2576(14)	5356(10)	3819(7)	41(7)
C(111)	-3841(16)	6126(12)	3921(9)	64(8)
C(112)	-4115(18)	7181(13)	4034(10)	70(9)
C(113)	-3151(22)	7463(14)	4107(10)	78(10)
C(114)	-1899(20)	6709(14)	4017(10)	71(11)
C(115)	-1623(15)	5686(11)	3873(8)	61(8)
C(120)	-2144(13)	3333(11)	4755(9)	45(7)
C(121)	-2076(16)	3844(12)	5377(10)	70(9)
C(122)	-1989(18)	3344(17)	6149(10)	91(11)
C(123)	-2010(16)	2352(15)	6311(10)	77(10)
C(124)	-2094(14)	1847(12)	5693(11)	66(8)
C(125)	-2128(13)	2334(11)	4911(8)	51(7)
C(130)	-3688(13)	4041(10)	3411(8)	37(7)
C(131)	-4528(16)	3660(11)	3886(10)	60(8)
C(132)	-5648(16)	3745(14)	3694(13)	74(10)
C(133)	-5969(15)	4276(14)	2968(12)	77(10)
C(134)	-5192(15)	4695(12)	2480(10)	67(8)
C(135)	-4022(15)	4573(12)	2680(9)	64(8)
C(210)	-3021(13)	-807(10)	1924(8)	42(7)
C(211)	-712(14)	-1587(11)	2301(9)	57(8)
C(212)	-83(18)	-2643(13)	2077(11)	79(10)
C(213)	951(17)	-2902(12)	1447(11)	68(9)
C(214)	1307(16)	-2119(14)	1072(10)	71(9)
C(215)	724(14)	-1704(11)	1293(9)	53(8)
C(220)	-2027(13)	452(10)	3216(7)	38(6)
C(221)	-3345(15)	905(12)	3402(8)	55(8)

TABLE 3 (continued)

Atom	x	y	z	U^a
C(222)	-3945(16)	726(13)	4212(9)	71(9)
C(223)	-325(19)	113(13)	4773(9)	68(10)
C(224)	-1933(18)	-335(14)	4589(10)	71(10)
C(225)	-1341(15)	-148(11)	3817(9)	57(8)
C(230)	-2346(13)	1138(11)	1533(7)	41(7)
C(231)	-2497(14)	581(12)	980(9)	55(8)
C(232)	-3411(17)	1046(14)	482(9)	64(9)
C(233)	-4227(15)	2073(15)	549(10)	61(9)
C(234)	-4139(14)	2699(12)	1067(10)	60(8)
C(235)	-3195(14)	2255(12)	1578(8)	50(8)
Cl(1) ^d	5813(7)	8928(6)	2038(6)	187(5)
Cl(2) ^d	5510(10)	7222(7)	1522(5)	206(7)
C(1*) ^d	6567(23)	7659(19)	1739(16)	172(18)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U tensor. ^b 20% occupancy metal atoms. ^c Hexane molecule. ^d Dichloromethane molecule.

TABLE 4

METAL-METAL BOND LENGTHS (Å) FOR HRuRh₃(CO)₁₂, HRuRh₃(CO)₁₀(PPh₃)₂, HRuCo₃(CO)₁₀(PPh₃)₂ AND HFeCo₃(CO)₁₀(PPh₃)₂ [12] (M = Co or Rh)

	HRuRh ₃ - (CO) ₁₂	HRuRh ₃ - (CO) ₁₀ (PPh ₃) ₂	HRuCo ₃ - (CO) ₁₀ (PPh ₃) ₂	HFeCo ₃ - (CO) ₁₀ (PPh ₃) ₂
Ru(1)-M(1)	2.726(6)	2.722(0)	2.656(2)	2.577(1) ^a
Ru(1)-M(2)	2.733(4)	2.724(0)	2.643(3)	2.577(1) ^a
Ru(1)-M(3)	2.878(5)	2.719(0)	2.640(2)	2.562(1) ^a
M(1)-M(2)	2.798(5)	2.802(0)	2.526(3)	2.515(1)
M(1)-M(3)	2.753(6)	2.733(0)	2.512(3)	2.498(1)
M(2)-M(3)	2.748(4)	2.789(0)	2.503(2)	2.487(1)

^a Corresponding Fe-Co bond lengths.

TABLE 5

SELECTED BOND ANGLES (°) FOR HRuRh₃(CO)₁₂, HRuRh₃(CO)₁₀(PPh₃)₂, HRuCo₃(CO)₁₀(PPh₃)₂ AND HFeCo₃(CO)₁₀(PPh₃)₂ [12] (M = Co or Rh)

	HRuRh ₃ - (CO) ₁₂	HRuRh ₃ - (CO) ₁₀ (PPh ₃) ₂	HRuCo ₃ - (CO) ₁₀ (PPh ₃) ₂	HFeCo ₃ - (CO) ₁₀ (PPh ₃) ₂
Ru(1)-M(1)-C(4)	79.2(1.4)	85.8(2)	76.7(4)	78.9(1) ^a
Ru(1)-M(2)-C(7)	91.5(1.2)	82.2(1)	77.4(6)	78.9(1) ^a
Ru(1)-M(3)-C(8)	110.0(1.2)	83.9(2)	76.3(5)	78.8(1) ^a
M(3)-M(1)-P(1)/C(5)	115.3(1.0)	117.0(0)	122.8(1)	122.5(0)
M(2)-M(1)-P(1)/C(5)	119.6(1.3)	124.0(0)	125.5(2)	125.4(0)
M(1)-M(2)-P(2)/C(5)	110.0(1.5)	122.1(0)	126.2(1)	126.7(0)
M(3)-M(2)-P(2)/C(6)	108.5(1.3)	118.7(0)	119.5(1)	120.0(0)
M(1)-M(3)-C(9)	100.1(1.4)	120.6(1)	122.4(4)	122.6(1)
M(2)-M(3)-C(9)	95.5(1.5)	120.8(1)	123.4(5)	123.2(1)
M(1)-Ru(1)-C(1)	100.2(1.3)	95.8(2)	102.6(4)	101.8(1)
M(1)-Ru(1)-C(3)	98.2(1.4)	101.2(2)	101.9(4)	100.8(1)
M(2)-Ru(1)-C(2)	100.2(1.5)	99.0(1)	99.5(6)	98.7(1)
M(2)-Ru(1)-C(3)	94.9(1.3)	101.3(1)	104.6(6)	103.9(1)
M(3)-Ru(1)-C(1)	109.0(1.4)	100.5(1)	98.7(4)	98.4(1)
M(3)-Ru(1)-C(2)	101.9(1.3)	99.1(1)	101.4(5)	102.1(1)

^a Corresponding Fe-Co-C bond angles.

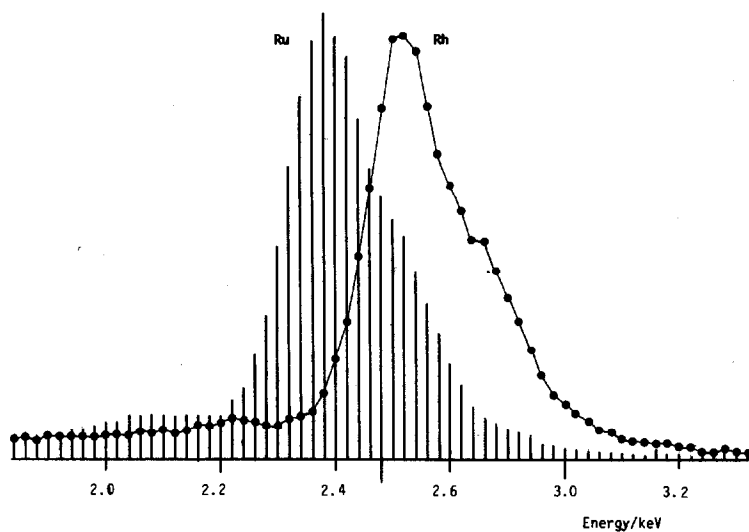


Fig. 6. X-ray fluorescence L-line spectra of pure ruthenium and rhodium.

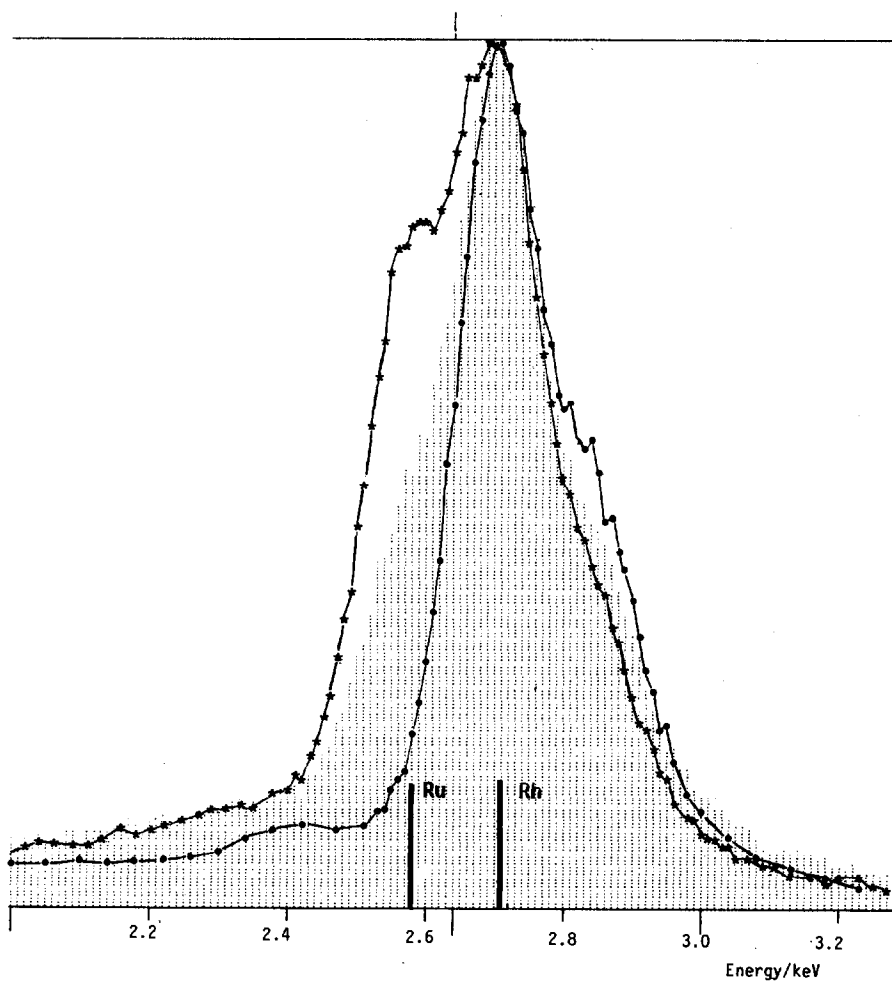


Fig. 7. X-ray fluorescence L-line spectra of $\text{HRuRh}_3(\text{CO})_{12}$ (dashed area), $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}$ (★) and $\text{Rh}_6(\text{CO})_{16}$ (●).

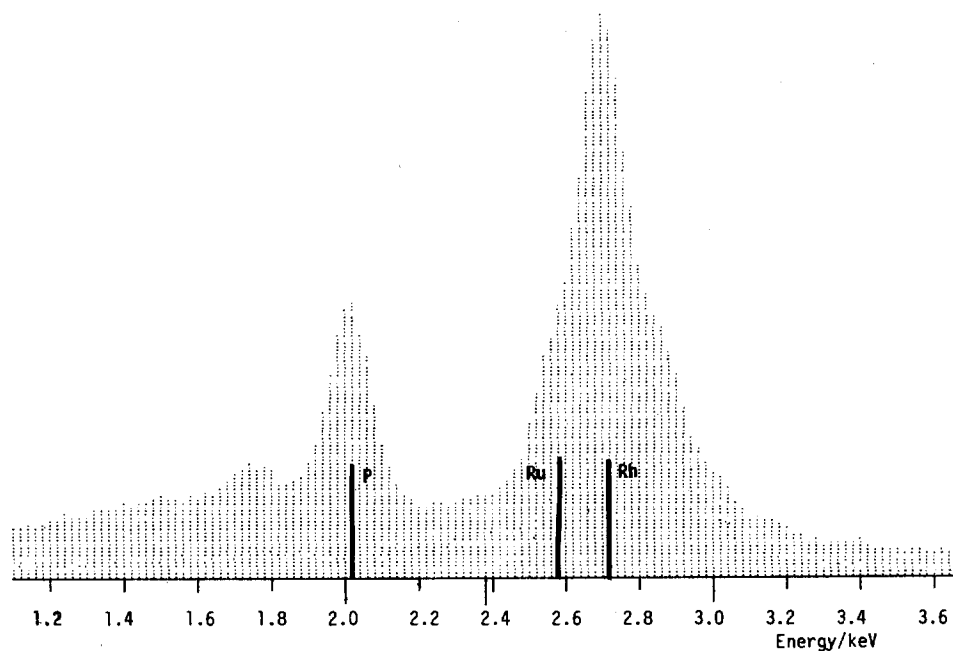


Fig. 8. X-ray fluorescence L-line spectrum of $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$.

as well. The size of the equatorial carbonyl angle of the Ru–Rh bond (Ru(1)–Rh(3)–C(8)), 110° , is similar to those of the corresponding angles in $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}$ (110.7 and 115.8°) and $\text{H}_2\text{Ru}_2\text{Co}_2(\text{CO})_{12}$ (111.2°) (see Table 5) [21]. The corresponding angles for the non-bridged bonds in the same clusters are $< 95^\circ$; in $\text{HRuRh}_3(\text{CO})_{12}$ the angles Ru(1)–Rh(1)–C(4) and Ru(1)–Rh(2)–C(7) are 79.2 and 91.5° , respectively. In $\text{Rh}_4(\text{CO})_{12}$ they have an intermediate value of 101.5° , but there is no corresponding bond lengthening. The Rh–Rh–C axial carbonyl angles (average 108.2°) are close to those found in clusters with no triply-bridging hydrogen atom: $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}$ (average 102.0°) and $\text{Rh}_4(\text{CO})_{12}$ (109.1°). The hydrogen opens the angles in $\text{H}_2\text{Ru}_2\text{Co}_2(\text{CO})_{12}$ to an average of 114.5° . Similar features can be observed for the phosphine derivatives of $\text{HRuRh}_3(\text{CO})_{12}$ and $\text{HRuCo}_3(\text{CO})_{12}$ from the data in Tables 4 and 5. Ligand replacement leads to a triply bridging hydrogen. The structures of $\text{HRuRh}_3(\text{CO})_{12}(\text{PPh}_3)_2$, $\text{HRuCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$ and $\text{HFeCo}_3(\text{CO})_{10}(\text{PPh}_3)_2$ are very similar.

X-ray fluorescence

An independent semiquantitative elemental analysis was made for ruthenium and rhodium by energy dispersive Electron Microprobe Analyser using emitted L-X-ray lines. Because of the small energy difference, the individual lines are not resolved, but the profiles of the line groups for pure elements are clearly separated (Fig. 6). In Figure 7 the measured L-line profile of $\text{HRuRh}_3(\text{CO})_{12}$ is shown, together with spectra obtained from $\text{H}_2\text{Ru}_2\text{Rh}_2(\text{CO})_{12}$ and $\text{Rh}_6(\text{CO})_{16}$. The resultant curve shapes reveal the presence of both ruthenium and rhodium. In addition a Ru/Rh ratio of less than 1/1 can be seen, and this, together with the known tetranuclear structure, establishes a 1/3 stoichiometry for the cluster core.

The measured L-line profile of $\text{HRuRh}_3(\text{CO})_{10}(\text{PPh}_3)_2$ (Fig. 8) is similar to that of the parent cluster, confirming that the same metal combination is present in both. The peak at 2.0 keV relates to phosphorus.

Acknowledgements

We thank the Neste Oy Foundation for financial support.

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